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Surface tension reduction (STR) in aqueous solutions of anionic surfactants with cobalt(III) complexes

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ABSTRACT

It has been observed that, at 25.0 ± 0.1 °C, $[Co(NH_3)_6](ClO_4)_3$, $[Co(en)_3](ClO_4)_3$, $[Co(bpy)_3](ClO_4)_3$, and $[Co(phen)_3](ClO_4)_3$ in the regions of 1.25–5.00 mM aqueous solutions cause a significant *surface tension reduction* (STR) of water by the surfactants, sodium dodecylsulfate (SDS) and sodium dodecylbenzenesulfonate (SBS), suggesting the formation of the 1:1 and 1:2 association complexes, $\{[complex]^{3+}(S^-)\}^{2+}$ and $\{[complex]^{3+}(S^-)_2\}^+$ where $[complex]^{3+} = [Co(NH_3)_6]^{3+}$, $[Co(en)_3]^{3+}$, $[Co(bpy)_3]^{3+}$, or $[Co(phen)_3]^{3+}$, $S^- = DS^-$ or BS^-. The effect of $[Co(en)_3]^{3+}$ on STR in SDS–water system is the largest due to a strong hydrophilic interaction between amino protons of $[Co(en)_3]^{3+}$ and sulfate oxygen atoms of DS^-. The effects of $[Co(en)_3]^{3+}$, $[Co(bpy)_3]^{3+}$, and $[Co(phen)_3]^{3+}$ on STR in SBS–water system are significant and almost same, meaning that the hydrophilic interaction between $[Co(en)_3]^{3+}$ and the sulfonate group is comparable to the hydrophobic interaction between $[Co(bpy)_3]^{3+}$ or $[Co(phen)_3]^{3+}$ and the phenyl group of BS^-. The Co(III) complexes of 1.25–5.00 mM are precipitated as $\{[complex]^{3+}(S^-)_3\}$ at 0.0295–0.173 mM of S^-. The precipitates, $\{[Co(bpy)_3]^{3+}(S^-)_3\}$ and $\{[Co(phen)_3]^{3+}(S^-)_3\}$ can be dissolved at higher molar ratio of $[S^-]/[complex^{3+}]$ than 3.5 for SDS and 4.0 for SBS. This observation suggests that the aggregated premicelle $[Co(bpy\ or\ phen)_3]_2(DS)_7^-$ or aggregated premicelle $[Co(bpy\ or\ phen)_3](BS)_4^-$ is formed.

1. Introduction

Studies on the surface tension of aqueous solutions of electrolytes, with or without surfactants, have been widely conducted. Yashiro et al. [1] measured the surface tension of aqueous solutions of cobalt(III) and nickel(II) complexes with diamine ligands which have a long alkyl chain (butyl, octyl, dodecyl, etc.) in water. They found that metal complexes with longer alkyl ligand chain reduced more significantly the surface tension of solutions. Ozeki et al. [2] in a study of the interaction of anionic surfactants with an Fe(II) complex, measured the surface tension of 0.05 mM $[Fe(phen)_3](ClO_4)_2$ (phen = 1,10-phenanthroline) aqueous solution at various concentrations of SDS. They found the initial decrease in surface tension is mainly induced by the formation and adsorption on the interface of a 1:1 association complex, $[Fe(phen)_3]^{2+}{\cdot}DS^-$, which was confirmed by a quantitative analysis of surface tension data in terms of the Gibbs adsorption isotherm [3]. Kratohvil et al. [4] measured the surface tension of SDS aqueous solutions with low concentrations (0.0200–0.800 mM) of $[Co(phen)_3]Cl_3$ and $[Co(bpy)_3]Cl_3$. They found that the addition of $[Co(phen)_3]Cl_3$ and $[Co(bpy)_3]Cl_3$ to the SDS solution reduced the surface tension and the critical micelle concentration (CMC) considerably. These findings differ from Ozeki et al. [2], who found that the addition of $[Fe(phen)_3]^{2+}$ to SDS solution did not influence CMC of SDS. Their finding was confirmed by the results of laser light scattering. Moreover, Ozeki et al. found that, at the SDS concentrations between the breakpoint (C_{pre}) and the micelle concentration (C_0), the premicellar aggregates, $[Fe(phen)_3]^{2+}{\cdot}2DS^-$ and $[Fe(phen)_3]^{2+}{\cdot}3DS^-$ were formed.

In order to classify the interactions between metal complex cations and anionic surfactants, we have investigated the interactions between Co(III) complexes and anionic surfactants on water surfaces when the concentrations of hydrophilic $[Co(NH_3)_6]^{3+}$ or $[Co(en)_3]^{3+}$ (en = ethylenediamine), and hydrophobic $[Co(bpy)_3]^{3+}$ (bpy = 2,2′-dipyiridyl) or $[Co(phen)_3]^{3+}$ complexes are relatively high (1.25–5.00 mM).

2. Materials and methods

2.1. Materials

Sodium dodecylsulfate, SDS (Wako, 95%), sodium dodecylbenzenesulfonate, SBS (Wako, 95%), and distilled water (Wako) were

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used as received. Co(III) perchlorate complexes were prepared according to literature methods [5–8] and were recrystallized from hot water.

Precipitates were isolated from the mixed solutions of Co(III) perchlorate complexes and higher concentration (>0.173 mM) of SDS or SBS by filtration. The compositions were determined by elemental analysis. $[Co(NH_3)_6](DS)_3 \cdot 7H_2O$: Found: C 40.11%, H 9.88%, N 7.72%. Calcd. for $C_{36}H_{107}N_6S_3O_{19}Co$ = C 39.91%, H 9.95%, N 7.76%. $[Co(en)_3](DS)_3 \cdot 3H_2O$: Found: C 46.82%, H 9.83%, N 7.75%. Calcd. for $C_{42}H_{105}N_6S_3O_{15}Co$ = C 46.30%, H 9.71%, N 7.71%. Precipitates of $[Co(NH_3)_6](BS)_3$, $[Co(en)_3](BS)_3$, $[Co(bpy)_3]$(DS or BS)$_3$, and $[Co(phen)_3]$(DS or BS)$_3$ were isolated but could not be analyzed due to their hygroscopicity.

2.2. *Surface tension measurements*

Surface tension was measured by the Wilhelmy plate technique at 25 ± 0.1 °C by Kyowa CBVP-Z tensiometer with Kyowa Temperature Controller 200. Concentrations were 1.25–5.00 mM for Co(III) perchlorate complexes and 0–50.0 mM for surfactants.

2.3. *Determination of solubility*

Absorbance at 469 nm of 1.25 mM hydrophilic $[Co(NH_3)_6](ClO_4)_3$ or $[Co(en)_3](ClO_4)_3$ and at 450 nm of 1.25 mM hydrophobic $[Co(bpy)_3](ClO_4)_3$ or $[Co(phen)_3](ClO_4)_3$ in various concentrations from 0.0150–50.0 mM of SDS or SBS were measured by Hitachi U-3410 spectrophotometer to determine solubility of Co(III) perchlorate complexes by using turbidity, in which the presence of precipitates showed high absorbance.

2.4. *NMR measurement*

^{1}H NMR spectra were recorded on Varian Mercury 300 spectrometer. The NMR measurements of mixtures of SDS or SBS and Co(III) perchlorate complexes were carried out in D_2O (Acros, 98%) and sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) as an internal standard.

3. Results and discussion

3.1. *Surface tensions in aqueous solutions of hydrophilic complexes, $[Co(NH_3)_6](ClO_4)_3$, $[Co(en)_3](ClO_4)_3$ and hydrophobic complexes, $[Co(bpy)_3](ClO_4)_3$ and $[Co(phen)_3](ClO_4)_3$ in aqueous solutions*

Surface tension of aqueous solutions of $[Co(NH_3)_6](ClO_4)_3$, $[Co(en)_3](ClO_4)_3$, $[Co(bpy)_3](ClO_4)_3$ and $[Co(phen)_3](ClO_4)_3$ plotted against molar concentration are shown in Fig. 1. All values are lower than that of pure water. This means a positive adsorption of solute on the water surface. From Fig. 1, surface tensions of the complexes in aqueous solutions are: $[Co(en)_3](ClO_4)_3 \geqslant [Co(NH_3)_6](ClO_4)_3 \gg [Co(phen)_3](ClO_4)_3 \cong [Co(bpy)_3](ClO_4)_3$. The difference may be attributed to $[Co(bpy)_3](ClO_4)_3$ and $[Co(phen)_3](ClO_4)_3$ being hydrophobic and are lacking polar N–H bonds, whereas $[Co(NH_3)_6](ClO_4)_3$ and $[Co(en)_3](ClO_4)_3$ are hydrophilic and have many polar N–H bonds.

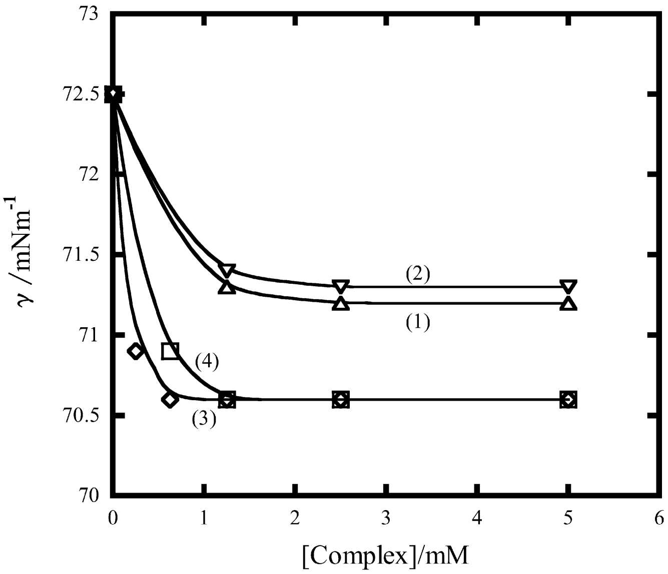


Fig. 1. Surface tension of aqueous solutions of $[Co(NH_3)_6](ClO_4)_3$, $[Co(en)_3](ClO_4)_3$, $[Co(bpy)_3](ClO_4)_3$, and $[Co(phen)_3](ClO_4)_3$ plotted against molar concentration: (1) $[Co(NH_3)_6](ClO_4)_3$ (△), (2) $[Co(en)_3](ClO_4)_3$ (▽), (3) $[Co(bpy)_3](ClO_4)_3$ (◇), and (4) $[Co(phen)_3](ClO_4)_3$ (□).

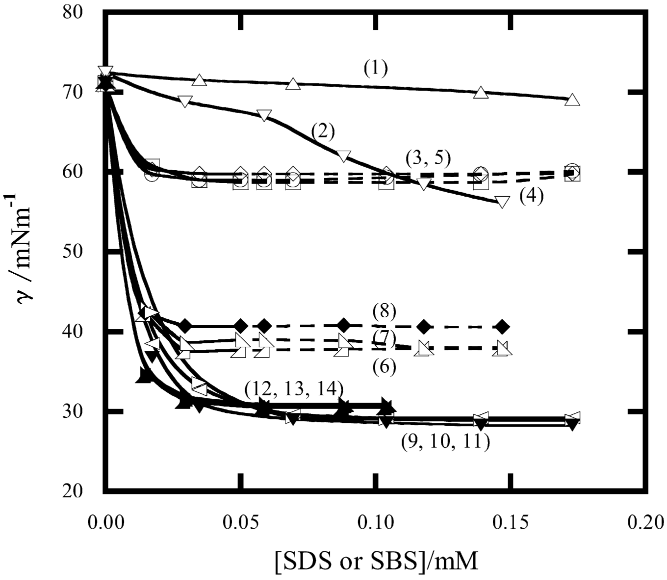


Fig. 2. Surface tension of aqueous solutions of SDS or SBS with or without 1.25–5.00 mM $[Co(NH_3)_6](ClO_4)_3$ or $[Co(en)_3](ClO_4)_3$ plotted against surfactant concentrations of 0–0.173 mM: (1) SDS (△), (2) SBS (▽), (3) 1.25 mM $[Co(NH_3)_6](ClO_4)_3$ + SDS (◇), (4) 2.50 mM $[Co(NH_3)_6](ClO_4)_3$ + SDS (□), (5) 5.00 mM $[Co(NH_3)_6](ClO_4)_3$ + SDS (○), (6) 1.25 mM $[Co(NH_3)_6](ClO_4)_3$ + SBS (◿), (7) 2.50 mM $[Co(NH_3)_6](ClO_4)_3$ + SBS (◺), (8) 5.00 mM $[Co(NH_3)_6](ClO_4)_3$ + SBS (◆), (9) 1.25 mM $[Co(en)_3](ClO_4)_3$ + SDS (◁), (10) 2.50 mM $[Co(en)_3](ClO_4)_3$ + SDS (▷), (11) 5.00 mM $[Co(en)_3](ClO_4)_3$ + SDS (▼), (12) 1.25 mM $[Co(en)_3](ClO_4)_3$ + SBS (▲), (13) 2.50 mM $[Co(en)_3](ClO_4)_3$ + SBS (◢), and (14) 5.00 mM $[Co(en)_3](ClO_4)_3$ + SBS (◣). Dashed line (- -) means that solution have slight turbidity. Solid line (—) means that solutions have no turbidity.

3.2. *Surface tension reduction (STR) in aqueous solutions of surfactants with hydrophilic complexes*

Fig. 2 shows surface tension of aqueous solutions of SDS or SBS with 1.25–5.00 mM $[Co(NH_3)_6](ClO_4)_3$ or $[Co(en)_3](ClO_4)_3$ plotted against surfactant concentrations of 0–0.173 mM. The area drawn with a solid line for the surface tension means there was a clear solution. On the other hand, the area drawn with a dotted line shows that there was slight turbidity. The addition of metal complex reduced the surface tension of SDS or SBS aqueous solutions. This tendency is the same as the result found by Ozeki et al. [2], who studied the interaction between $[Fe(phen)_3]^{2+}$ and SDS. So, the decrease of the surface tension at dilute concentrations of surfactants (0–0.05 mM SDS or SBS) with high concentrations of complexes (1.25–5.00 mM $[Co(NH_3)_6](ClO_4)_3$ or $[Co(en)_3(ClO_4)_3]$ can be explained by the formation of the 1:1 and 1:2 association com-

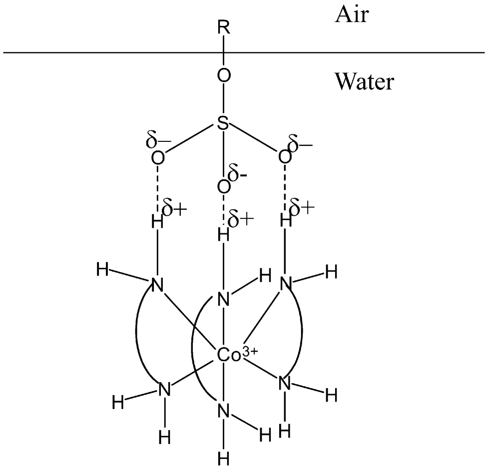


Fig. 3. An interaction model between $[Co(en)_3]^{3+}$ and DS^- ($R = CH_3\text{-}(CH_2)_{11}\text{-}$).

plexes, $\{[complex]^{3+}(S^-)\}^{2+}$ and $\{[complex]^{3+}(S^-)_2\}^{+}$ and their adsorption on the water surface. The breakpoints of surface tension curves with concentration of $[Co(NH_3)_6](ClO_4)_3$ or $[Co(en)_3](ClO_4)_3$ appeared at ca. 0.03 mM of SDS or SBS. In the region of concentrations of SDS or SBS higher than 0.03 mM, the surface tension curves flattened out. This can be interpreted as showing that the adsorption of association complexes on the water surface in this region has reached saturation.

$$[complex]^{3+} + S^- \rightleftharpoons \{[complex]^{3+}(S^-)\}^{2+}, \tag{1}$$

$$\{[complex]^{3+}(S^-)\}^{2+} + S^- \rightleftharpoons \{[complex]^{3+}(S^-)_2\}^{+}, \tag{2}$$

$$\{[complex]^{3+}(S^-)_2\}^{+} + S^- \rightleftharpoons \{[complex]^{3+}(S^-)_3\} \tag{3}$$

$$complex = [Co(NH_3)_6]^{3+} \text{ or } [Co(en)_3]^{3+},$$

$$S^- = DS^- \text{ or } BS^-.$$

The flattened out values on the surface tension curves for $[Co(NH_3)_6](ClO_4)_3$ solutions with surfactants, which are ca. 60 $mN\,m^{-1}$ for SDS and ca. 40 $mN\,m^{-1}$ for SBS, are relatively higher than those on $[Co(en)_3](ClO_4)_3$, which are ca. 29 $mN\,m^{-1}$ for SDS and ca. 31 $mN\,m^{-1}$ for SBS. This result suggests that $[Co(en)_3]^{3+}$ cation interacts more strongly with dodecylsulfate (DS^-) or dodecylbenzenesulfonate (BS^-) than does $[Co(NH_3)_6]^{3+}$ due to a strong hydrophilic interaction between amino protons of $[Co(en)_3]^{3+}$ and sulfate or sulfonate oxygen atoms of anionic surfactants. We postulate the interaction model according to Masuda et al. [9], which is shown in Fig. 3. According to this model, such an association between a surfactant anion and $[Co(en)_3]^{3+}$ cation along a C_3 axis makes a close arrangement of surfactants on the water interface due to a significant reduction of electric repulsion among surfactant anions. Therefore, the reduction of electric repulsion causes the higher adsorption of anionic surfactants on air–water interface. The curves of surface tension of (3) for 1.25 mM $[Co(NH_3)_6](ClO_4)_3$, (4) for 2.50 mM $[Co(NH_3)_6](ClO_4)_3$ and (5) for 5.00 mM $[Co(NH_3)_6](ClO_4)_3$ with SDS in Fig. 2 almost overlap, and the curves of surface tension of (6) for 1.25 mM $[Co(NH_3)_6](ClO_4)_3$, (7) for 2.50 mM $[Co(NH_3)_6](ClO_4)_3$ and (8) for 5.00 mM $[Co(NH_3)_6](ClO_4)_3$ with SBS in Fig. 2 almost overlap. Analogous results were also obtained for $[Co(en)_3](ClO_4)_3$ with SDS or SBS. These results can be interpreted as showing that the equilibria (1) and (2) are completely shifted to the right due to the high concentrations of complexes (1.25–5.00 mM) compared with surfactant (less than 0.0500 mM). Therefore, the surface tensions in aqueous solutions of the surfactants with different concentrations of a complex are almost same.

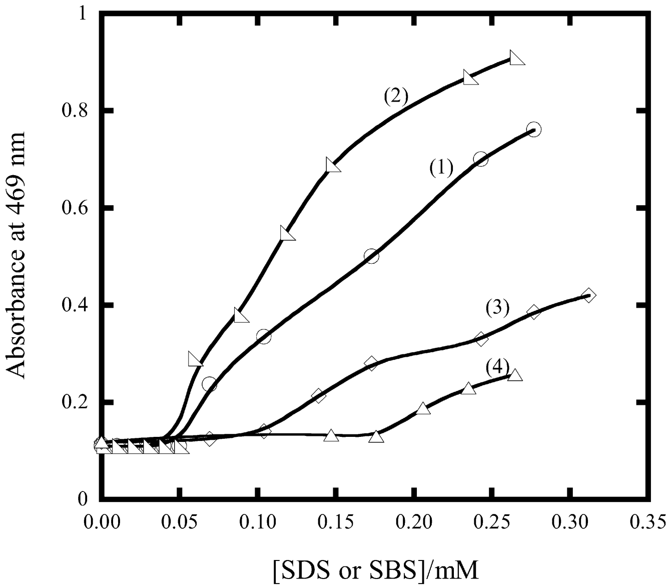


Fig. 4. The change of absorbance at 469 nm of aqueous solutions of 1.25 mM $[Co(NH_3)_6](ClO_4)_3$ or $[Co(en)_3](ClO_4)_3$ with the various concentrations of SDS or SBS: (1) 1.25 mM $[Co(NH_3)_6](ClO_4)_3$ + SDS (○), (2) 1.25 mM $[Co(NH_3)_6](ClO_4)_3$ + SBS (◺), (3) 1.25 mM $[Co(en)_3](ClO_4)_3$ + SDS (◇), and (4) 1.25 mM $[Co(en)_3](ClO_4)_3$ + SBS (△).

3.3. Turbidities of mixed solutions of metal complexes with surfactants

Fig. 4 shows the change of absorbance at 469 nm (where the ligand-field transition band of the Co(III) complexes are observed) of aqueous solutions of 1.25 mM $[Co(NH_3)_6](ClO_4)_3$ or $[Co(en)_3](ClO_4)_3$ with the various concentrations of SDS or SBS. The increase of absorption at 469 nm in comparison to that without surfactants means light scattering by turbidity occurred. In the case of $[Co(NH_3)_6]^{3+}$, the absorbance at 469 nm increased with the increase of surfactant concentrations at more than 0.0500 mM of the surfactants, meaning that $[Co(NH_3)_6]$(DS or BS)$_3$ precipitates are not generated below 0.0500 mM of SDS or SBS. On the other hand, for $[Co(en)_3]^{3+}$, the absorbance at 469 nm increased from 0.100 mM of SDS or from 0.173 mM of SBS, meaning that $[Co(en)_3]$(DS or BS)$_3$ was not deposited below 0.100 mM of SDS or below 0.173 mM of SBS. At concentrations of surfactant higher than 0.173 mM, yellow precipitates of the surfactant salts of Co(III) complexes were deposited. These precipitates have the compositions of $[Co(NH_3)_6](DS)_3 \cdot 7H_2O$ and $[Co(en)_3](DS)_3 \cdot 3H_2O$ which were determined by elemental analysis. The other precipitates, $[Co(NH_3)_6](BS)_3$ and $[Co(en)_3](BS)_3$, were not analyzed due to their hygroscopicity. On the other hand, $[Co(bpy)_3]^{3+}$ or $[Co(phen)_3]^{3+}$ are easily deposited with DS^- or BS^- but the precipitates dissolve in excess DS^- or BS^- (from over averaged molar ratio 3.5 of [SDS]/[complex] or 4.0 of [SBS]/[complex]).

Fig. 5 shows the absorbance changes of 1.25 mM $[Co(bpy)_3](ClO_4)_3$ or $[Co(phen)_3](ClO_4)_3$ solution with the various concentrations of the surfactants at 450 nm where there is a ligand-field transition band. The increase of the absorbance with the increase of the SDS or SBS concentration is observed in the region from 0.0295 mM ($\log(C/M) = -4.53$) to 0.347 mM ($\log(C/M) = -3.46$) of surfactants. It can be inferred that the increase of absorbance due to turbidity of precipitates starts in this region. In the next region from 0.347 mM of SDS or SBS to the average ratio ([surfactant]/[complex]) lower than 3.5 of SDS or 4.0 of SBS, yellow precipitates of $[Co(bpy)_3]$(DS or BS)$_3$ or $[Co(phen)_3]$(DS or BS)$_3$ were observed. It was impossible to measure the absorbance changes in this region due to the high density of precipitates.

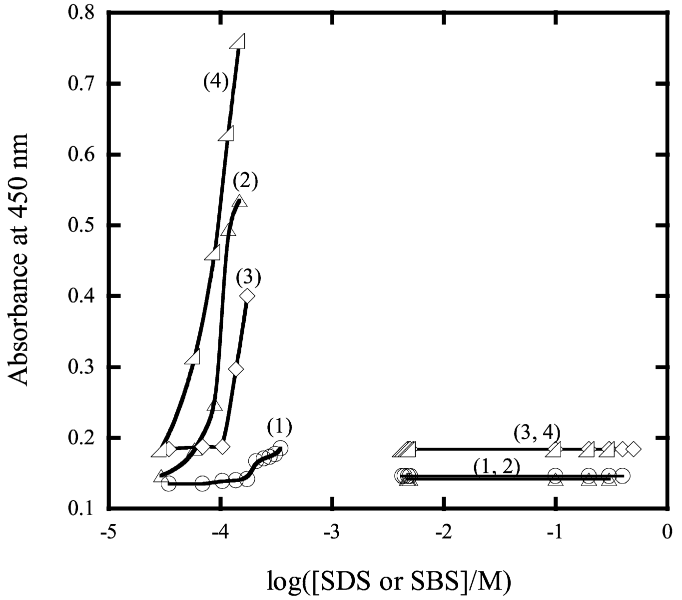


Fig. 5. The change of absorbance at 450 nm of aqueous solutions of 1.25 mM $[Co(bpy)_3](ClO_4)_3$ or $[Co(phen)_3](ClO_4)_3$ with the various concentrations of SDS or SBS: (1) 1.25 mM $[Co(bpy)_3](ClO_4)_3$ + SDS (○), (2) 1.25 mM $[Co(bpy)_3](ClO_4)_3$ + SBS (△), (3) 1.25 mM $[Co(phen)_3](ClO_4)_3$ + SDS (◇), and (4) 1.25 mM $[Co(phen)_3](ClO_4)_3$ + SBS (⊿).

Table 1
Molar ratio of complexes and surfactants on dissolving precipitation.

Complexes	[complex] (mM)	[SDS] (mM)	Ratio of [SDS]/[complex]	Average of ratio
$[Co(bpy)_3](ClO_4)_3$	1.25	4.62	3.7	
	2.50	8.00	3.2	3.4
	5.00	16.5	3.3	
$[Co(bpy)_3](ClO_4)_3$	1.25	4.25	3.4	
	2.50	9.50	3.8	3.8
	5.00	20.50	4.1	
$[Co(phen)_3](ClO_4)_3$	1.25	4.62	3.7	
	2.50	8.00	3.2	3.5
	5.00	17.5	3.5	
$[Co(phen)_3](ClO_4)_3$	1.25	4.25	3.4	
	2.50	8.50	3.4	3.8
	5.00	22.5	4.5	

In the case of $[Co(bpy)_3]^{3+}$ or $[Co(phen)_3]^{3+}$ with SDS, the absorbance at 450 nm increased with the increase of SDS concentration at more than 0.138 mM, meaning that the $[Co(bpy\ or\ phen)_3](DS)_3$ precipitate is not generated below 0.138 mM of SDS. On the other hand, for $[Co(bpy)_3]^{3+}$ or $[Co(phen)_3]^{3+}$ with SBS, the absorbance at 450 nm increased at more than 0.0590 mM of SBS due to the deposition of $[Co(bpy\ or\ phen)_3](BS)_3$. At concentrations of SDS higher than 0.138 mM or that of SBS higher than 0.0590 mM to the averaged ratio mentioned above, yellow precipitates of $[Co(bpy)_3](DS\ or\ BS)_3$ or $[Co(phen)_3](DS\ or\ BS)_3$ were observed. At the ratio ([surfactant]/[complex]) more than 3.5 of SDS or 4.0 of SBS as indicated in Table 1, the precipitates dissolved due to the formation of aggregated premicelle $[Co(bpy\ or\ phen)_3]_2(DS)_7^-$ for the complexes with SDS or aggregated premicelle $[Co(bpy\ or\ phen)_3](BS)_4^-$ for those with SBS.

Kratohvil et al. [4] measured the absorbance of $[Co(bpy)_3]^{3+}$ and $[Co(phen)_3]^{3+}$ with SDS. The measured concentrations of the complexes and those of SDS were 0.0600–0.500 mM and 0.0316–3.16 mM, respectively. They found that at low concentrations of the added trivalent cations and at higher temperatures, SDS dissolved forming micelles. At higher concentrations of $[Co(bpy)_3](ClO_4)_3$ and $[Co(phen)_3](ClO_4)_3$ the orange liquid phase separated. Their observations differ from ours because the complex concentrations are different. The concentrations of Co(III) complexes in this study are 10–100 times higher than Kratohvil's. Therefore, the precipitates, $[Co(bpy\ or\ phen)_3](DS)_3$ or $[Co(bpy\ or\ phen)_3](BS)_3$, are formed in the region from 0.138 mM of SDS (or 0.0590 mM of SBS) to the average ratio ([surfactant]/[complex]) lower than 3.5 of SDS (or 4.0 of SBS).

3.4. ^1H NMR spectra on hydrophobic complexes with surfactants in D_2O

Table 2 shows ^1H NMR chemical shift (δ/ppm) of SDS, SBS, $[Co(bpy)_3](ClO_4)_3$, $[Co(phen)_3](ClO_4)_3$ and the mixtures of $[Co(bpy)_3](ClO_4)_3$ or $[Co(phen)_3](ClO_4)_3$ with SDS or SBS in D_2O. The ^1H NMR of 5.00 mM $[Co(bpy)_3]^{3+}$ shows $\delta = 7.44$, 7.76, 8.52 and 8.81 due to H_a, H_b, H_c and H_d protons of $[Co(bpy)_3]^{3+}$ whereas the ^1H NMR of 5.00 mM $[Co(phen)_3]^{3+}$ shows $\delta = 7.64$, 7.91, 9.06 and 8.47 due to $H_{a'}$, $H_{b'}$, $H_{c'}$ and $H_{d'}$ protons of $[Co(phen)_3]^{3+}$, respectively. The addition of an excess of SDS solution (more than 3.5 molar ratio of [SDS]/[complex]) to $[Co(bpy)_3]^{3+}$ or $[Co(phen)_3]^{3+}$ results in little change in chemical shifts of bpy and phen protons. On the other hand, the addition of an excess of SBS solution (more than 4.0 molar ratio of [SBS]/[complex]) to $[Co(bpy)_3]^{3+}$ or $[Co(phen)_3]^{3+}$ induces significant changes of chemical shifts of bpy or phen protons: $H_a = 7.44 \rightarrow 7.27$, $H_b = 7.76 \rightarrow 7.53$, $H_c = 8.52 \rightarrow 8.18$, $H_d = 8.81 \rightarrow 8.64$ for the bpy complex; $H_{a'} = 7.64 \rightarrow 7.52$, $H_{b'} = 7.91 \rightarrow 7.76$, $H_{c'} = 9.06 \rightarrow 8.71$, $H_{d'} = 8.47 \rightarrow 8.10$ for the phen complex. These higher-field shifts mean that there are aromatic intermolecular interactions (π–π stacking) [10,11] between the aromatic ring of SBS and those of bpy or phen on forming aggregated premicelle $[Co(bpy\ or\ phen)_3]_2(DS)_7^-$ or $[Co(bpy\ or\ phen)_3](BS)_4^-$.

3.5. Surface tension reduction (STR) in aqueous solutions of surfactants with hydrophobic complexes

Figs. 6 and 7 show surface tension of aqueous solutions of SDS or SBS with 1.25–5.00 mM $[Co(bpy)_3](ClO_4)_3$ and $[Co(phen)_3](ClO_4)_3$ plotted against surfactant concentrations of 0.0150–50.0 mM, respectively. Significant amounts of precipitates were observed in the range from 0.173 mM to the average ratio ([surfactant]/[complex]) lower than 3.5 of SDS or 4.0 of SBS, so that surface tension in this range cannot be measured. The addition of $[Co(bpy)_3](ClO_4)_3$ or $[Co(phen)_3](ClO_4)_3$ into SDS or SBS solution in the range of 0.0150–0.173 mM lowers the surface tensions significantly meaning that $[Co(bpy)_3]^{3+}$ or $[Co(phen)_3]^{3+}$ forms 1:1 and 1:2 association complexes with SDS or SBS and positively adsorb on the water surface.

$$[complex]^{3+} + S^- \rightleftharpoons \{[complex]^{3+}(S^-)\}^{2+}, \tag{4}$$

$$\{[complex]^{3+}(S^-)\}^{2+} + S^- \rightleftharpoons \{[complex]^{3+}(S^-)_2\}^{+}, \tag{5}$$

$$\{[complex]^{3+}(S^-)_2\}^{+} + S^- \rightleftharpoons \{[complex]^{3+}(S^-)_3\}, \tag{6}$$

$$2\{[complex]^{3+}(S^-)_3\} + S^- \rightleftharpoons \{[complex]_2^{3+}(S^-)_7\}^{-}, \tag{7}$$

$$\{[complex]^{3+}(S^-)_3\} + S^- \rightleftharpoons \{[complex]^{3+}(S^-)_4\}^{-}, \tag{8}$$

$$complex = Co(bpy)_3 \text{ or } Co(phen)_3,$$

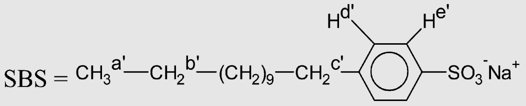
$$S^- = DS^- \text{ or } BS^-.$$

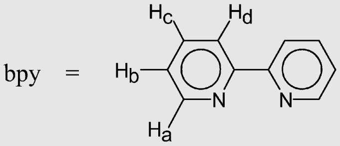
The surface tension of SDS aqueous solution with $[Co(bpy)_3](ClO_4)_3$ or $[Co(phen)_3](ClO_4)_3$ is higher than that of SBS. This result indicates that the interaction between the complexes and SBS is stronger than that of SDS. The SBS structure contains hydrophobic aromatic rings and alkyl chain whereas that of SDS contains the only alkyl chains. So, SBS is more hydrophobic than SDS.

Table 2
^{1}H NMR chemical shifts in D_2O.

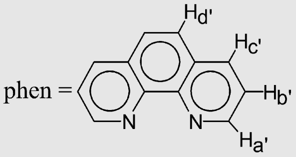
Compounds	a (a')	c (c')	d (d')	(e')	H_a ($H_{a'}$)	H_b ($H_{b'}$)	H_c ($H_{c'}$)	H_d ($H_{d'}$)
50.0 mM SDS	0.88 (t)	1.67 (q)	4.02 (t)					
50.0 mM SBS	–	2.42 (b)	7.11 (d)	7.69 (d)				
5.00 mM $[Co(bpy)_3](ClO_4)_3$ (1)					7.44 (d)	7.76 (t)	8.52 (t)	8.81 (d)
5.00 mM $[Co(phen)_3](ClO_4)_3$ (2)					7.64 (d)	7.91 (t)	9.06 (d)	8.47 (s)
(1) + 50.0 mM SDS	0.82 (t)	1.59 (q)	3.96 (t)		7.49 (d)	7.81 (t)	8.54 (t)	8.89 (d)
(1) + 50.0 mM SBS	–	2.35 (b)	7.09 (b)	7.71 (b)	7.27 (d)	7.53 (t)	8.18 (t)	8.64 (d)
(2) + 50.0 mM SDS	0.82 (t)	1.62 (q)	4.00 (t)		7.73 (d)	7.99 (t)	9.08 (d)	8.49 (s)
(2) + 50.0 mM SBS	–	2.39 (b)	7.16 (b)	7.71 (b)	7.52 (d)	7.76 (b)	8.71 (d)	8.10 (s)

SDS = $CH_3^{a}—CH_2^{b}—(CH_2)_8—CH_2^{c}—CH_2^{d}—OSO_3^{-}Na^{+}$





(1) $[Co(bpy)_3](ClO_4)_3$



(2) $[Co(phen)_3](ClO_4)_3$

Abbreviations in parentheses are: s = singlet, d = doublet, t = triplet, q = quintet and b = broad.

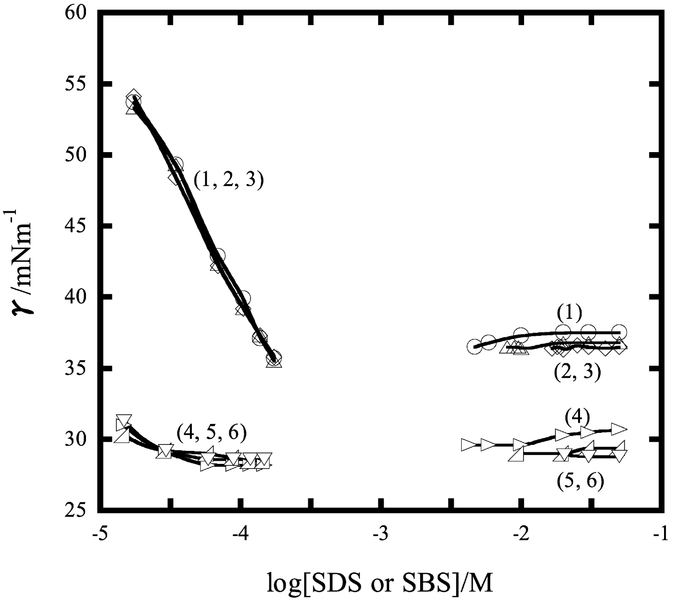


Fig. 6. Surface tension of aqueous solutions of SDS or SBS with 1.25–5.00 mM $[Co(bpy)_3](ClO_4)_3$ plotted against surfactant concentrations of 0.0150–50.0 mM: (1) 1.25 mM $[Co(bpy)_3](ClO_4)_3$ + SDS (○), (2) 2.50 mM $[Co(bpy)_3](ClO_4)_3$ + SDS (△), (3) 5.00 mM $[Co(bpy)_3](ClO_4)_3$ + SDS (◇), (4) 1.25 mM $[Co(bpy)_3](ClO_4)_3$ + SBS (▷), (5) 2.50 mM $[Co(bpy)_3](ClO_4)_3$ + SBS (◺), and (6) 5.00 mM $[Co(bpy)_3](ClO_4)_3$ + SBS (▽).

$[Co(bpy)_3]^{3+}$ or $[Co(phen)_3]^{3+}$ complexes also have hydrophobic aromatic rings. Therefore, the hydrophobic aromatic ring of SBS can interact more strongly with those of the complexes than SDS to form association complexes. The curves of surface tension of (1) for 1.25 mM $[Co(bpy)_3](ClO_4)_3$, (2) for 2.50 mM $[Co(bpy)_3](ClO_4)_3$ and (3) for 5.00 mM $[Co(bpy)_3](ClO_4)_3$ with SDS in Fig. 6 almost overlap, and the curves of surface tension of (4) for 1.25 mM $[Co(bpy)_3](ClO_4)_3$, (5) for 2.50 mM $[Co(bpy)_3](ClO_4)_3$ and (6) for 5.00 mM $[Co(bpy)_3](ClO_4)_3$ with SBS in Fig. 6 also overlap. Analogous results were also obtained for $[Co(phen)_3](ClO_4)_3$ with SDS or SBS as shown in Fig. 7. These results can be interpreted as mentioned above for $[Co(NH_3)_6]^{3+}$ and $[Co(en)_3]^{3+}$. The equilibria (4) and (5) are completely shifted to the right due to the high concentration of complexes (1.25–5.00 mM) compared with surfactant (less than 0.0500 mM). Therefore, the surface tensions of the surfactants with different concentrations of a complex are almost the same. Surface tension of aqueous solutions of SDS or SBS with 1.25–5.00 mM $[Co(bpy)_3](ClO_4)_3$ or $[Co(phen)_3](ClO_4)_3$ in the range of $-2.36 < \log[\text{surfactant}] < -1.30$ was also examined. The hydrophobic interaction of SBS with $[Co(bpy)_3]^{3+}$ or $[Co(phen)_3]^{3+}$ in the region is stronger than that of SDS. Figs. 6 and 7, in the region of log[surfactant] from −2.36 to −1.30, show the surface tensions to be larger than the minima in the region of log[surfactant] from −4.82 to −3.76. The minima of surface tension from −4.06 to −3.76 corresponds to the adsorption of $\{[Co(bpy\ or\ phen)_3]^{3+}(DS^{-}\ or\ BS^{-})_2\}^{+}$ on the water surface and the surface tension from −2.36 to −1.30 corresponds to the adsorption of $\{[Co(bpy\ or\ phen)_3]_2^{3+}(DS^{-})_7\}^{-}$ or $\{[Co(bpy\ or\ phen)_3]^{3+}(BS^{-})_4\}^{-}$. The difference may be attributed to the difference of premicelle size.

3.6. The comparison on STRs in aqueous solutions of surfactants with complexes

Figs. 8 and 9 show the comparison on surface tensions of 0–0.173 mM SDS and SBS aqueous solutions, respectively with 2.50 mM $[Co(NH_3)_6]^{3+}$, $[Co(en)_3]^{3+}$, $[Co(bpy)_3]^{3+}$ and $[Co(phen)_3]^{3+}$ aqueous solutions. Fig. 8 shows that the effect of $[Co(en)_3]^{3+}$ on surface tension reduction in aqueous solution of SDS is largest due to a strong hydrophilic interaction between amino protons of $[Co(en)_3]^{3+}$ and sulfate oxygen atoms of DS^{-}. On the other hand, the effects of $[Co(en)_3]^{3+}$, $[Co(bpy)_3]^{3+}$, and $[Co(phen)_3]^{3+}$ on STR in aqueous solution of SBS as shown in Fig. 9, are significant and almost same, meaning that the hydrophilic interaction between $[Co(en)_3]^{3+}$ and sulfonate group is comparative to the hydrophobic interaction between $[Co(bpy)_3]^{3+}$ or $[Co(phen)_3]^{3+}$ and phenyl group of BS^{-}.

4. Summary

The study on the effects of Co(III) complexes on the STR in aqueous solutions of the surfactants (SDS and SBS), revealed that the hydrophilic complexes, $[Co(NH_3)_6]^{3+}$ and $[Co(en)_3]^{3+}$ (en =

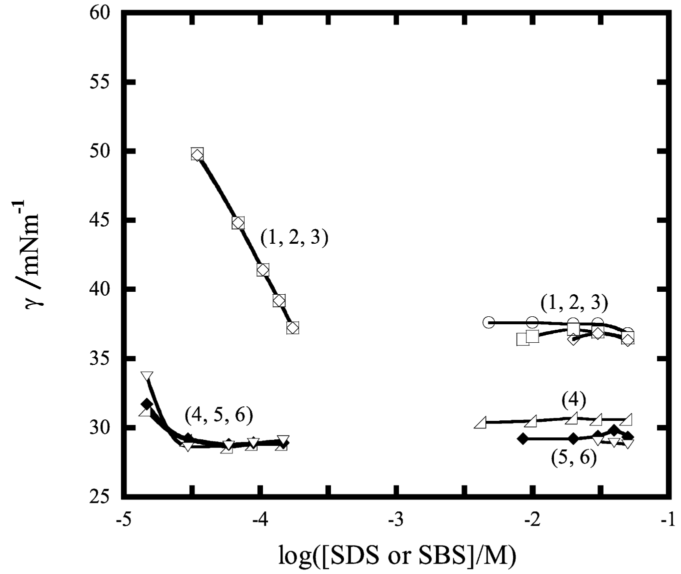


Fig. 7. Surface tension of aqueous solutions of SDS or SBS with 1.25–5.00 mM $[Co(phen)_3](ClO_4)_3$ plotted against surfactant concentrations of 0.0150–50.0 mM: (1) 1.25 mM $[Co(phen)_3](ClO_4)_3$ + SDS (○), (2) 2.50 mM $[Co(phen)_3](ClO_4)_3$ + SDS (□), (3) 5.00 mM $[Co(phen)_3](ClO_4)_3$ + SDS (◇), (4) 1.25 mM $[Co(phen)_3](ClO_4)_3$ + SBS (◿), (5) 2.50 mM $[Co(phen)_3](ClO_4)_3$ + SBS (◆), and (6) 5.00 mM $[Co(phen)_3](ClO_4)_3$ + SBS (▽).

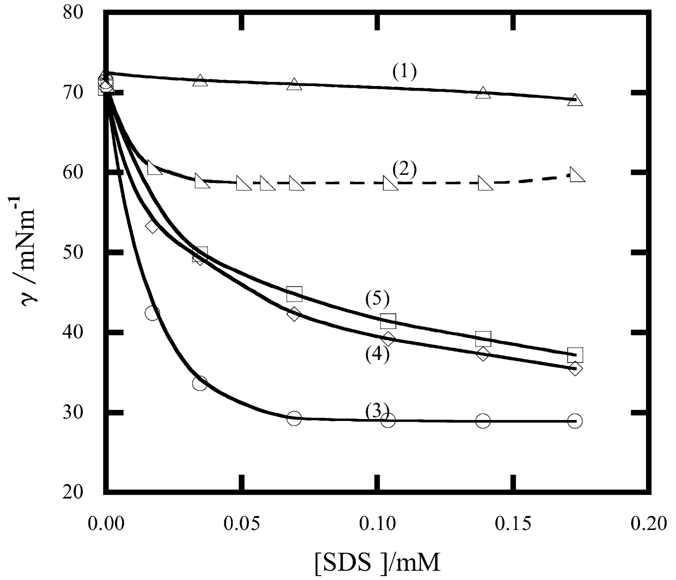


Fig. 8. Comparison on surface tensions of 0–0.173 mM SDS aqueous solutions, with 2.50 mM $[Co(NH_3)_6]^{3+}$, $[Co(en)_3]^{3+}$, $[Co(bpy)_3]^{3+}$ and $[Co(phen)_3]^{3+}$ aqueous solutions, respectively. (1) SDS (△), (2) 2.50 mM $[Co(NH_3)_6](ClO_4)_3$ + SDS (◺), (3) 2.50 mM $[Co(en)_3](ClO_4)_3$ + SDS (○), (4) 2.50 mM $[Co(bpy)_3](ClO_4)_3$ + SDS (◇), and (5) 2.50 mM $[Co(phen)_3](ClO_4)_3$ + SDS (□).

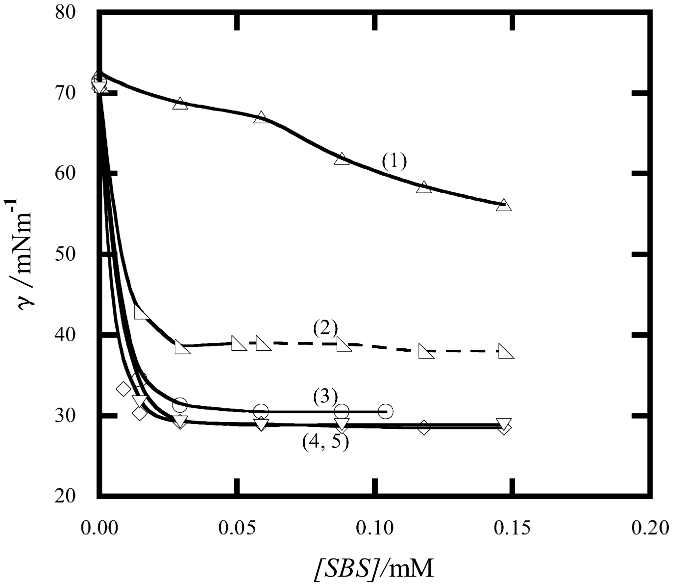


Fig. 9. Comparison on surface tensions of 0–0.173 mM SBS aqueous solutions, with 2.50 mM $[Co(NH_3)_6]^{3+}$, $[Co(en)_3]^{3+}$, $[Co(bpy)_3]^{3+}$ and $[Co(phen)_3]^{3+}$ aqueous solutions, respectively. (1) SBS (△), (2) 2.50 mM $[Co(NH_3)_6](ClO_4)_3$ + SBS (◺), (3) 2.50 mM $[Co(en)_3](ClO_4)_3$ + SBS (○), (4) 2.50 mM $[Co(bpy)_3](ClO_4)_3$ + SBS (◇), and (5) 2.50 mM $[Co(phen)_3](ClO_4)_3$ + SBS (▽).

ethylenediamine) and the hydrophobic complexes, $[Co(bpy)_3]^{3-}$-(bpy = 2,2′-dipyridyl) and $[Co(phen)_3]^{3+}$ (phen = 1,10-phenanthroline) cause a significant STR in aqueous solutions of the surfactants, suggesting the formation and adsorption of the 1:1 and 1:2 association complexes, $\{[complex]^{3+}(S^-)\}^{2+}$ and $\{[complex]^{3+}(S^-)_2\}^+$. The effect of $[Co(en)_3]^{3+}$ on STR in aqueous solutions of SDS is the largest due to a strong hydrophilic interaction between amino protons of $[Co(en)_3]^{3+}$ and sulfate oxygen atoms of DS^-. The effects of $[Co(en)_3]^{3+}$, $[Co(bpy)_3]^{3+}$, and $[Co(phen)_3]^{3+}$ on STR in aqueous solutions of SBS are significant and almost the same, meaning that the hydrophilic interaction between $[Co(en)_3]^{3+}$ and the sulfonate group is comparable to the hydrophobic interaction between $[Co(bpy)_3]^{3+}$ or $[Co(phen)_3]^{3+}$ and the phenyl group of BS^-. The Co(III) complexes are precipitated as $\{[complex]^{3+}(S^-)_3\}$ at 0.0295–0.173 mM of SDS or SBS. The precipitates, $\{[Co(bpy)_3]^{3+}(S^-)_3\}$ and $\{[Co(phen)_3]^{3+}(S^-)_3\}$ can be dissolved at the higher molar ratio of $[S^-]/[complex^{3+}]$ than 3.5 for SDS and 4.0 for SBS. This observation suggests that the aggregated premicelle $[Co(bpy\ or\ phen)_3]_2(DS)_7^-$ or $[Co(bpy\ or\ phen)_3](BS)_4^-$ is formed.

The significant STR in aqueous solutions of the surfactants with the Co(III) complexes is not dependent on the complex concentrations since the complex concentration is extraordinary high (1.25–5.00 mM) compared with surfactants (less than 0.05 mM), meaning that the association complexes, $\{[complex]^{3+}(S^-)\}^{2+}$ and $\{[complex]^{3+}(S^-)_2\}^+$ are completely formed and their adsorption on the water surface is saturated at more than 0.05 mM of the surfactants.

In conclusions, this study clearly classifies the two types of interactions between metal complexes cations and anionic surfactants. One is a hydrophilic interaction, where an electrostatic interaction between hydrophilic metal complexes and anionic surfactants is dominant. Another is a hydrophobic interaction to form aggregated premicelle of hydrophobic metal complexes and anionic surfactants. The largest STR in aqueous solutions of the hydrophilic interaction in $[Co(en)_3]^{3+}$-DS^- system is almost equal to that of the hydrophobic interaction in $[Co(bpy\ or\ phen)_3]^{3+}$-$BS^-$ one.

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